Dual-Curable Acrylic Pressure-Sensitive Adhesives Based on UV and Thermal Processes

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Abstract: Several dual-curable acrylic pressure-sensitive adhesives (PSA) were synthesized by the radical polymerization of acrylic monomers containing benzophenone, hydroxyl, and alkyl groups. The optimum extent of UV-induced cure was determined by varying the content of the benzophenone groups (the photoinitiator) from 0.5 to 1.5 wt%. The weight average molecular weight of the polymers obtained ranged from 300,000 to 700,000 amu. The coated pressure-sensitive adhesives were cured either by short UV exposure to induce the grafting of acrylic polymers, or by heating for 6 h at 60 °C to promote the reactions between the polyisocyanates and hydroxyl groups. The dual-curing behavior was determined by monitoring both processes quantitatively by infrared spectroscopy. The developed dual-curable acrylic pressure-sensitive adhesives were found to compensate for the limitations in UV-induced curing of thick coatings.

Keywords: pressure-sensitive adhesives, acrylic, cure/hardening, UV, polyurethane.

Introduction

Pressure-sensitive adhesives (PSAs) are almost indispensable in everyday life, being used for labels, tapes, films, and other special adhesive applications.[1-4] The demand for the radiation-curable acrylic PSA type of solvent-based acrylic copolymers has been increasing in recent years due to fast production rates and promising new properties of chemical cross-linking bonding.[5] Usually a radiation-curable acrylic PSA that can be cured with UV light contains a photoinitiator group. This photoinitiator can be directly incorporated in the main chain of the polymer, with the advantage of having no low-molecular-weight residues that are often responsible for a strong odor and also can result in adhesion failures after cross-linking.[6,7]

The main drawback of radiation-curable PSAs has been the curing thickness being limited to approximately 100 μm due to filtering of the UV light.[8] Attempts to overcome this problem have introduced a cationic cross-linking mechanism into the radiation-curable PSA. Radiation-cationic-curable PSAs can be cured for thicknesses of 1-2,000 μm, but they still exhibit problems such as slow curing and being expensive.[9,10] The limitation of the curable-coating

thickness in radiation-curable PSAs has prompted us to study dual-curable PSAs that combine UV irradiation and thermal curing processes. This system contains two types of reactive functions: (1) a UV-curable functional group (a photoinitiator) and (2) a thermally curable functional group (polyols to react with the polyisocyanate).

In this study, several acrylic copolymers for dual-curable PSAs have been synthesized by the radical polymerization of acrylic monomers including benzophenone, hydroxyl, and alkyl groups. The synthesized acrylic copolymers were formulated with a polyisocyanate cross-linker to yield dual-curable PSAs. The dual-curing processes of the prepared PSAs were monitored quantitatively by infrared spectroscopy. We also studied the effect of coating thickness on the extent of UV-induced cure, and assessed the extent to which the additional thermal curing compensated for the limited UV-induced curing in thick coatings.

Experimental

Materials and Synthesis. 2-Ethylhexyl acrylate (2-EHA), 2-hydroxyethyl methacrylate (2-HEMA), acrylic acid, dimethylaminoethyl methacrylate, benzophenone, and 2,2'-azodiisobutyronitrile (AIBN) were purchased from Aldrich Chemical. An acrylic photoinitiator (4-benzophenone dieth-

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yleneglycol acrylate) was obtained from SK Cytec (Korea), and a chain transfer agent (trimethylolpropane tri(3-mercaptopropionate)) was supplied by Bruno Bock Chemische Fabrik (Mannheim, Germany).

A typical dual-curable PSA was synthesized according to the following procedure. Ethyl acetate (286 g) was placed into a 1 liter four-necked flask equipped with a reflux condenser, stirrer, thermometer, and nitrogen inlet, and heated to 80 °C. The monomer mixture of 2-ethylhexyl acrylate (58.1 g), 2-hyroxyethyl methacrylate (20.21 g), butyl acrylate (202. 63g), acrylic acid (8.0 g), 4-benzophenone diethyleneglycol acrylate (1.374 g) and trimethylolpropane tri(3-mercaptopropionate) (0.1 g) including 1.59 g of AIBN in acetone (18.2 g) was slowly added over 4 h. The reaction mixture was maintained at 80 °C for 5 h and cooled to room temperature. The solid content of the polymer solution was 55 wt% from the gravimetric method (120 °C oven × 30 min).

Measurements. The molecular weights of the synthesized dual-curable PSA were estimated by size exclusion chromatography, using two Waters Styragel (HR 3 and HR 4) columns that connected to a M930 solvent delivery module and a RI 750F refractive-index (RI) detector (Younglin Instrument Co., Korea). The mobile phase was HPLC grade tetrahydrofuran and calibration was with near-monodisperse polystyrene standards purchased from Polyscience Inc.

Depth profiles of the extent of UV-induced cure at the adhesive-substrate interface were obtained by FT-IR/ATR spectroscopy (Spectrum GX, Perkin Elmer). The spectrometer was equipped with a 45°-cut ATR crystal made from ZnSe, and the number of scans was 128 with a resolution of 8 cm^{-1}. The calculated absorbance was treated as an average over a penetration depth of approximately 2.0 μm. Samples with adhesive-coating thicknesses from 20 to 100 μm were prepared. The adhesive was coated on the quartz surface using different drawing-bar coaters, and the opposite side of the adhesive was in contact with the ATR crystal to obtain the FT-IR signals. The samples were exposed through the quartz to the UV radiation from a metal-halide lamp (EFOS UV system) via a fiber optic guide. The UV-B dose at samples was 29 mW/cm^2 over the wavelength range from 280 to 320 nm.

Samples for testing the PSA properties were prepared as follows. The prepared acrylic copolymers and their blends with the polyisocyanate cross-linker were poured on corona-treated PET films. They were coated by a bar coater at thicknesses of 50, 62.3, and 75.0 μm, dried for 5 min at 80 °C, UV irradiated, and then aged for 24 h at 60 °C. The adhesive strength was measured according to the ASTM D3654 method (H5KS, Tinus Olsen) using a peel angle and rate of 180° and 300 mm/min, respectively. The probe tack-displacement behaviors of the synthesized PSAs were measured using a texture analyzer (Micro Stable Systems, TA-XT2i) with a stainless-steel cylinder probe with a diameter

of 10 mm. The measurements were carried out at separation rates of 10 mm/sec under a constant pressure of 100 gf/cm^2 and a dwell time of 1 sec at room temperature.

Results and Discussion

Synthesis of Dual-Curable Acrylic Copolymers for PSAs. Several dual-curable acrylic copolymers having hydroxyl, benzophenone, and alkyl groups for PSA were synthesized by solution radical polymerization as shown in Figure 1. 4-Benzophenone diethyleneglycol acrylate was directly incorporated into the polymer main chain as an acrylated photoinitiator, which provided the advantage of having no low-molecular-weight residues after cross-linking. The synthesis recipes of the dual-curable acrylic copolymers for PSAs are summarized in Table I. To obtain the optimum extent of UV-induced cure, the concentration of the benzophenone group was varied from 0.5 to 1.5 wt%. As Czech reported, increasing the acrylated photoinitiator content greatly increases the viscosity of a dual-curable acrylic copolymer.[11,12] Therefore, we controlled the molecular weight and solvent viscosity of the acrylic copolymers using different concentrations of the chain transfer agent, trimethylolpropane tri(3-mercaptopropionate) (0.03-0.06% w/w). The weight average molecular weights of the obtained polymers ranged from 300,000 to 700,000.

The synthesized acrylic polymers were formulated with a polyisocyanate cross-linker (Coronate L, Nippon Polyurethane Industry, Japan) to give a dual-curable PSA. After evaporating the solvent by brief heating, the coated PSAs were cured either by a short UV exposure to induce the cross-linking of acrylic polymers, or by heating for 6 h at 60 °C to promote the reactions of the polyisocyanates and the hydroxyl groups. Both processes were monitored quantitatively by infrared spectroscopy to evaluate the dual-curing behaviors, because this technique allows the chemical modifications induced in PSA coatings by UV radiation or heat to be monitored accurately.

Effect of Coating Thickness on the Extent of UV-Induced Cure. Figure 2 shows a schematic of the photocuring mechanism of radiation-curable PSAs.[11] Upon UV irradiation of
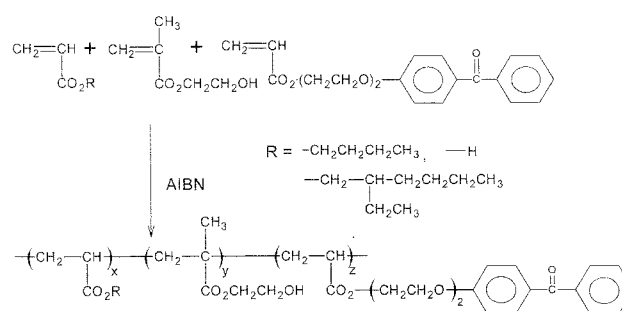

Figure 1. Radical polymerization of acrylic monomers for dual-curable acrylic copolymers.

Table I. Recipes for the Synthesis of Dual-Curable Acrylic Copolymers for PSAs. PI, Photoinitiator

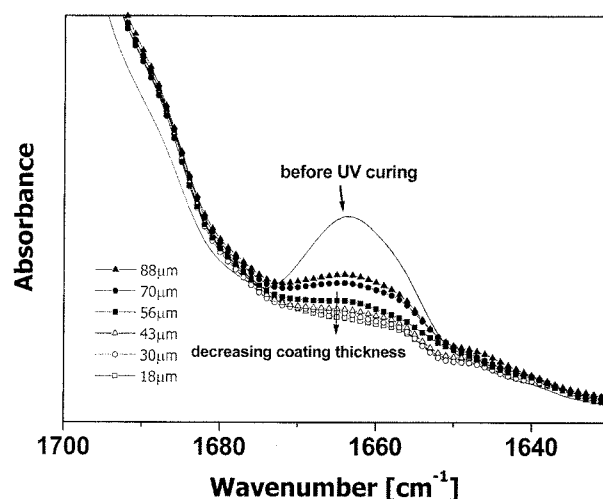| Ingredient	Reactor Charge			
	PI (0.5 wt%)	PI (0.5 wt%) + Amine	PI (1.0 wt%)	PI (1.5 wt%)
2-EHA	58.1	58.1	58.1	58.1
2-HEMA	20.21	20.21	20.21	20.21
Butyl acrylate	202.63	202.63	202.63	202.63
Acrylic acid	8	8	8	8
4-Benzophenone diethylene glycol acrylate	1.374	1.314	2.748	4.122
Trimethylopropane tri(3-mercaptopropionate)	0.1	0.1	0.2	0.2
Dimethylaminoethyl methacrylate[a]		0.687		
AIBN/acetone	1.59/18.2	1.59/18.2	1.59/18.2	1.59/18.2
Ethyl acetate	286	286	286	286

[a]Dimethylaminoethyl methacrylate was used as an amine synergist for the benzophenone-initiated UV curing.
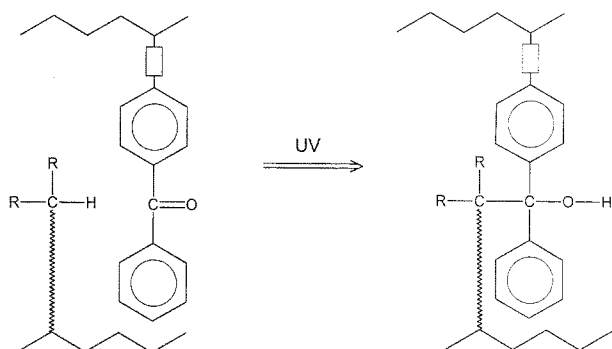
Figure 2. A schematic representation of the photochemical cross-linking induced by UV irradiation.[11]

Figure 3. Carbonyl absorption of the copolymerized benzophenone groups at the bottom of layers before and after an UV irradiation for various coating thicknesses.

the acrylic PSA, the excited carbonyl groups of the benzophenone moiety extract protons from the polymer backbone, and then recombines with carbon-centered radicals to produce cross-linking networks in the adhesive. The copolymerized benzophenone groups are converted during the UV-induced photochemical reaction of the acrylic adhesive. Therefore, the conversion of the benzophenone groups can be investigated by observation of their characteristic absorption band at 1663 cm^{-1} (ν for C=O). However, the amount of photoinitiator (0.5-1.5 wt%) in the above synthesized PSA is too small to detect the carbonyl absorption peaks in our synthesized acrylic copolymers. We therefore added 2 wt% benzophenone into the 1.0 wt% acrylic copolymer to investigate the change of carbonyl peak during UV irradiation. Although this was not a real-time method, the changes in the absorption could be followed successfully due to the absence of post reactions.

Figure 3 shows the carbonyl absorption variations of the benzophenone in the synthesized acrylic PSA before and after UV curing at the bottom of coatings with different thicknesses. The carbonyl absorption peak in the synthe-

sized PSAs containing 2 wt% benzophenone was clearly evident at 1663 cm^{-1} before UV irradiation. In our experiment, the UV dose was fixed at 29 mW/cm^2 over the wavelength range from 280 to 320 nm. Figure 3 reveals that the absorption of the benzophenone groups at the bottom of the layer gradually decreased with decreasing thickness of the coating. The intensity of UV light which is transmitted through a layer with a certain absorption is decreased in relation to the Beer-Lambert law. With increasing absorption, i.e. with increasing the coating thickness, the remaining intensity rapidly drops down. This internal-filter effect of the benzophenone groups leads to an increasing retardation of the reaction with increasing thickness of the coating. Integration of the peak area of the carbonyl absorption in Figure 3 can be converted to the percentage benzophenone conversion as a function of coating thickness.
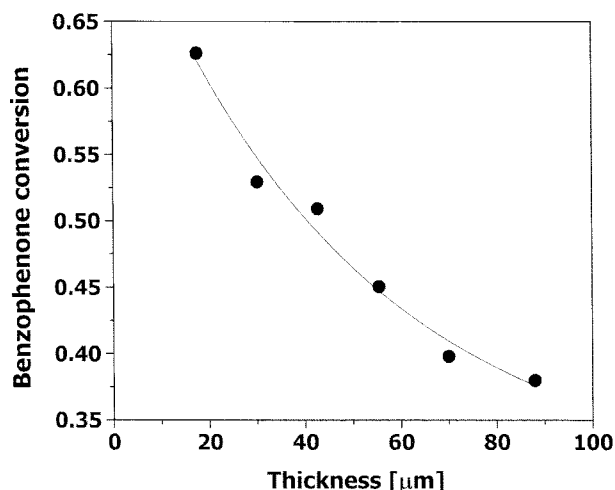
Figure 4. Depth profile of the conversion of the externally added benzophenone after UV irradiation at 29 mW/cm^2 over the wavelength range from 280 to 320 nm.

Figure 5. Isocyanate IR absorption of the dual-curable PSAs containing 1.5 wt% polyisocyanate cross-linker (Coronate L) for heating at 60 °C for up to 6 h.

Figure 4 shows the benzophenone-group conversions after the UV irradiation as a function of coating thickness. The conversion of benzophenone groups gradually decreased with increasing coating thickness, with the maximum UV curing thickness limited to 100 μm in our experiments. Scherzer *et al.* previously reported data of the conversion of the copolymerized benzophenone group at various depths,[13,14] and similarly showed that the conversion of the benzophenone groups gradually decreased with the increasing coating thickness. We therefore hypothesized that the insufficient UV curing exhibited by thick coatings could be compensated by additional thermal curing.

Thermal Curing Behaviors of the Dual-Curable Acrylic PSAs. We also monitored the thermal curing reactions that generate the polyurethane network in the dual-curable PSAs with infrared spectroscopy. Polyisocyanate at 1.5 wt% was added to the PSA formulations because of a slow curing reaction. A 28-μm-thick film was applied onto a quartz crystal and heated at 60 °C for 6 h. After removing the solvent (which represented 55 wt% of the solid content of the formulation), IR spectra were taken at regular time intervals using the FT-IR-ATR spectrometer.

Figure 5 shows the differential spectra obtained after subtraction of the IR spectrum of the uncured sample. The spectra are characterized by the disappearance of the 2270 cm^{-1} band that is characteristic of stretching modes of the isocyanate (-NCO) group. It was found that the thermal curing required to produce polyurethane networks was slower than expected. The thermal curing process for the quantitative conversion required heating at 60 °C for at least 6 h. The UV curing process of the PSA required exposure to UV light for only short periods (of the order of several seconds), as is typical for the curing conditions at the line speeds used. The results of IR experiments indicated that
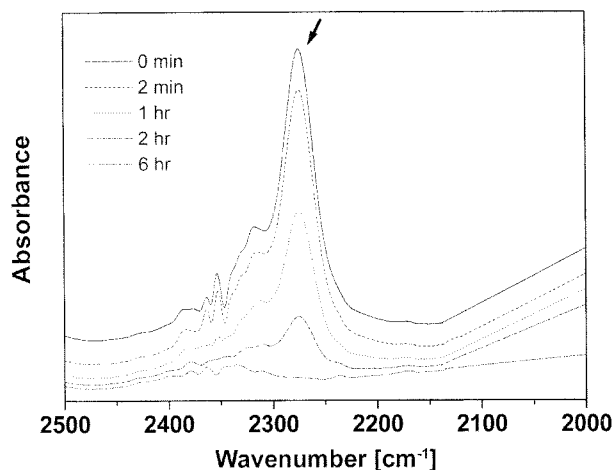
heating from the UV lamp did not significantly contribute to the reactions of polyisocyanates and hydroxyl groups.

Adhesion Properties of the Dual-Curable Acrylic PSAs for Differing Curing Processes. The required coating thickness depends on the application of a PSA, and is typically in the range from 10 to about 130 μm. The degree of adhesion to both the adhesive substrate and the opposite side as well as the adhesive properties depend on the degree of cure and its spatial distribution over the profile of the coating, with a homogeneous through cure of the adhesive being essential to attaining optimum properties. Table II summarizes the 180°-peel adhesion strength of the dual-curable PSAs as functions of coating thickness and curing process (UV curing only or UV plus thermal curing).

It is known that the adhesive becomes more cohesive in a typical PSA formulation as the more polymer chains undergo the cross-linking reaction, while their adhesions decrease. Figure 6 shows the effects of photoinitiator concentration on the peel adhesion strength in the PSA samples cured using UV only. The content of benzophenone photoinitiator was varied from 0.5 to 1.5 wt%. Figure 6 shows that the peel adhesion strength of PSA samples with only UV curing increased markedly with the coating thickness due to the insufficient curing of thick coatings. Moreover, increasing the photoinitiator content from 0.5 to 1.5 wt% did not improve the homogeneity of the cured networks in thicker coatings. This tendency was greater when the concentration of the photoinitiator was higher, due to its UV absorption. These observation were supported by the above depth-profile experiments showing that the conversion of the benzophenone group gradually decreased with increasing coating thickness (Figure 4). In order to increase the UV-induced cure rate, we also prepared PSA formulations containing an amine synergist, which is generally required for benzophe-

Table II. Adhesion Strength (for a 180° peel) of the Dual-Curable PSAs as Functions of the Coating Thickness and Curing Process (UV Curing Only and UV+Thermal Curing)

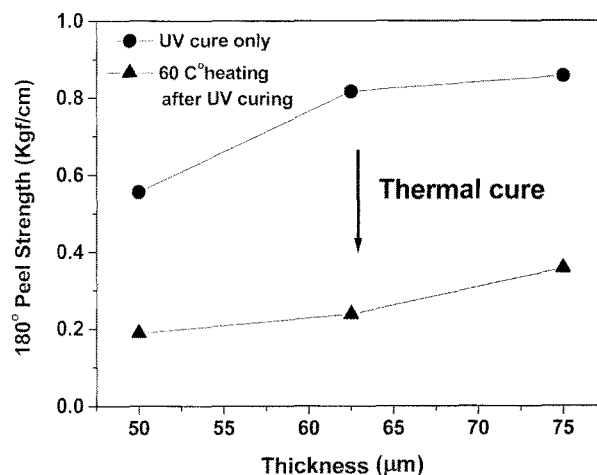| PI[a] Content (wt%)	Coating Thickness (μm)	Adhesion (kgf/cm) for UV Curing Only	Adhesion (kgf/cm) for UV+Thermal Curing After 1 h	Adhesion (kgf/cm) for UV+Thermal Curing After 24 h
0.5	50.0	0.73861	0.29929	0.16837
	62.5	0.75932	0.69502	0.13664
	75.0	0.83600	0.87114	0.20607
1.0	50.0	0.55549	0.29716	0.18882
	62.5	0.81637	0.32041	0.23734
	75.0	0.85682	0.58732	0.35742
1.5	50.0	0.41485	0.34924	0.19375
	62.5	1.03110	0.57983	0.30274
	75.0	1.09254	0.63907	0.38809
0.5 + Amine	50.0	0.46559	0.20743	0.41570
	62.5	1.53025	0.25111	0.34721
	75.0	1.00739	0.32753	0.43982

[a]4-Benzophenone diethyleneglycol acrylate was used as a PI (photo initiator) for the benzophenone-initiated UV curing.
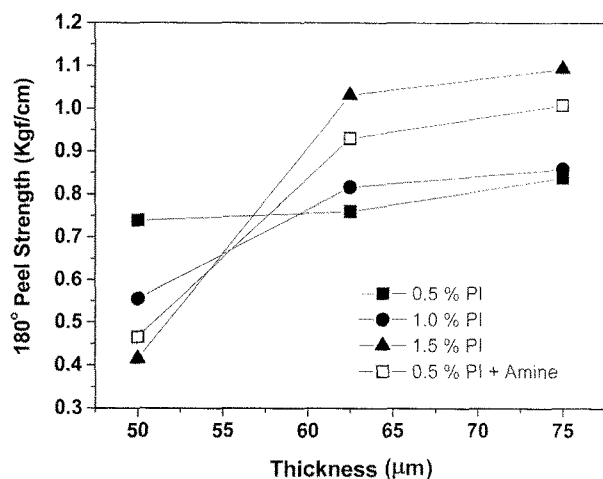
Figure 6. Effects of photoinitiator (PI) concentration on the peel adhesion strength of PSA samples cured with UV-B irradiation of 29 mW/cm².

Figure 7. Peel adhesion strength of dual-curable PSAs containing 1.0 wt% PI as a function of the curing process (UV cure only and UV + thermal cure).

none or other hydrogen-extracting photoinitiators, and studied the effects on UV curing behaviors for different coating thicknesses. However, Figure 6 indicates that the amine synergist had little effect in our experiments with thick UV-cured coatings. It is assumed that the amine synergist had no effective on the UV curing at the bottom of thick layers, but is helpful for the surface curing due to the regeneration of strongly propagating free radicals from weak peroxide radicals.[15]

Figure 7 shows the peel adhesion strength as a function of the curing process (UV curing only and UV plus thermal curing). The peel adhesion strength was lower for the UV-cured samples followed by the subsequent thermal curing

than for those cured with UV only. As the polymer chains undergo the cross-linking reactions, the adhesive becomes more cohesive and the generated cross-linked connections inhibit extensively the mobility of the polymer. The decreased peel adhesion strength of UV plus thermal cured samples can be explained by this inhibited mobility of the polymer chains. Moreover, the peel adhesion strength of UV plus thermal cure samples was not markedly affected by the coating thickness. This implies that a dual-curable PSA based on UV and thermal processes exhibits a more homogeneous cross-linking network than a PSA cured with UV only as the coating thickness increases.

It has been known that the tack of polymer is decreased
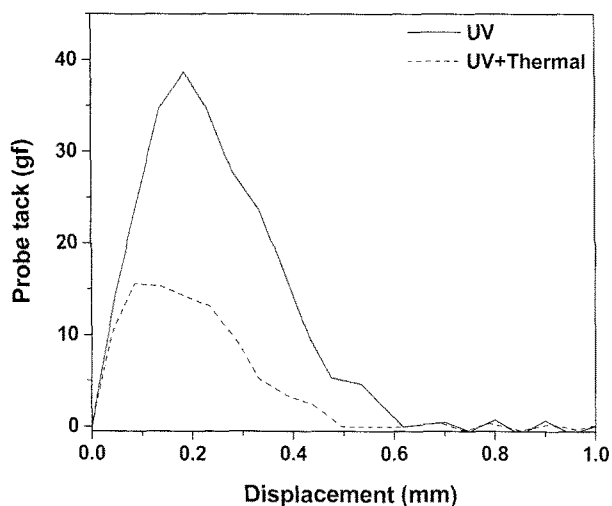
Figure 8. Probe tack-displacement curves of 75 μm thick coating PSAs films containing 1.0 wt% PI, as a functions of the curing process (UV cure only and UV+thermal cure).

by the degree of cross-linking.[16] Figure 8 shows the effects of the curing process on probe tack-displacement behaviors of dual-curable PSAs. Initial peak height and displacement to debonding are the key features of the profile. The height of the initial peak depends on the ability of the PSA to wet the probe surface and the amount resistance it can exert against the tack. Figure 8 shows that the probe tack strength of the UV plus thermal cure sample was lower then that of the UV only cure sample. The reduced probe tack strength of UV plus thermal cure sample may be due to the increased cross-linking networks between PSAs polymer chains relative to the UV only cure sample. From these results we conclude that the additional thermal curing of the developed dual-curable acrylic PSAs compensated for the limited UV curing in thick coatings.

Conclusions

In the present study, several dual-curable acrylic PSAs were synthesized by radical solution polymerization of acrylic monomers including benzophenone, hydroxyl, and alkyl groups. The PSAs were cured either by a short UV

exposure to induce the cross-linking of the acrylic polymers, or by heating for 6 h at 60 °C to promote the reactions of the polyisocyanates and hydroxyl groups. The curing processes were quantitatively monitored by infrared spectroscopy to evaluate the UV and thermal curing behaviors. The developed dual-curable acrylic PSAs based on both UV and thermal processes results in a homogeneous through cure of the adhesive that overcomes the insufficient UV curing in thick coatings.

References

(1) J. K. Kim, J. W. Kim, M. I. Kim, and M. S. Song, *Macromol. Res.*, **14**, 517 (2006).

(2) D. Satas, in *Handbook of Pressure Sensitive Adhesive Technology*, D. Satas, Ed., Van Nostrand Reinhold, New York, 1999, pp 1-21.

(3) I. Benedek, and L. J. Heymans, in *Pressure Sensitive Adhesive Technology*, Marcel Dekker, New York, 1997, pp 1-3.

(4) D. V. Varanese, *Adhesives Age*, **4**, 2 (2000).

(5) R. Malik, *RadTech Report*, May/June, **25** (2001).

(6) Y. B. Kim, H. K. Kim, and J. W. Hong, *J. Appl. Polym. Sci.*, **102**, 5566 (2006).

(7) J. D. Cho and J. W. Hong, *Macromol. Res.*, **13**, 362 (2005).

(8) A. Dobman, in *New Development and Applications in UV Curable Hotmelt Pressure Sensitive Adhesives*, Afera Seminar, Netherlands, September (2002).

(9) K. Studer, C. Decker, E. Beck, and R. Schwalm, *Eur. Polym. J.*, **41**, 157 (2004).

(10) C. Decker, F. Masson, and R. Schwalm, *Macromol. Mater. Eng.*, **288**, 17 (2003).

(11) Z. Czech, *Eur. Polym. J.*, **40**, 2221 (2004).

(12) Z. Czech, *J. Appl. Polym. Sci.*, **87**,1354 (2003).

(13) K. H Schumacher, H. Lim, and T. Tsukamoto, *Proceedings of RadTech Asia*, **512** (2003).

(14) T. Scherzer, A. Tauber, and R. Mehnert, *Vibrational Spectroscopy*, **29**, 125 (2002).

(15) N. S. Allen, M. S. Johnson, P. K. T. Oldering, and S. Salim, in *Chemistry & Technology of UV & EB Formulation for Coatings, Inks & Paints*, P. K. T. Oldring, Ed., SITA Technology, 1991, Vol. 2, pp 153-156.

(16) A. Zoel, *J. Adhesion*, **34**, 201 (1991).